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(54) Zirconium alloy products and fabrication processes.

(57) Modifying standard Zircaloy alloy processing techniques by limiting the working and annealing temperatures utilized after conventional beta treatment results in Zircaloy alloy product having superior high temperature steam corrosion resistance.

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sometimes considered as an alloying element rather than an impurity, since it is a solid solution strengthener of zirconium.

Nuclear grade Zircaloy-2 or Zircaloy-4 alloys
5 are made by repeated vacuum consumable electrode melting to produce a final ingot having a diameter typically between 16 and 25 inches. The ingot is then conditioned to remove surface contamination, heated into the beta, alpha + beta phase or high temperature alpha phase and
10 then worked to some intermediate sized and shaped billet. This primary ingot breakdown may be performed by forging, rolling, extruding or combinations of these methods. The intermediate billet is then beta solution treated by heating above the alpha + beta/beta transus temperature
15 and then held in the beta phase for a specified period of time and then quenched in water. After this step it is further thermomechanically worked to a final desired shape at a temperature typically below the alpha/alpha + beta transus temperature.

20 For Zircaloy material that is to be used as tubular cladding for fuel pellets, the intermediate billet may be beta treated by heating to approximately 1050°C and subsequently water quenched to a temperature below the alpha + beta to alpha transus temperature.

25 Depending upon the size and shape of the intermediate product at this stage of fabrication, the billet may first be alpha worked by heating it to about 750°C and then forging the hot billet to a size and shape appropriate for extrusion. Once it has attained the desired size
30 and shape (substantially round cross-section), the billet is prepared for extrusion. This preparation includes drilling an axial hole along the center line of the billet, machining the outside diameter to desired dimensions, and applying a suitable lubricant to the surfaces of the billet. The billet diameter is then reduced by extrusion
35 at 700°C or greater through a frustoconical die and over a mandrel. The as-extruded cylinder may then be optionally

The alpha matrix itself may be characterized by a heavily cold worked or dislocated structure, a partially recrystallized structure or a full recrystallized structure, depending upon the type of final anneal given the material.

Where final material of a rectangular cross section is desired, the intermediate billet may be processed substantially as described above, with the exception that the reductions after the beta solution treating process are typically performed by hot, warm and/or cold rolling the material at a temperature within the alpha phase or just above the alpha to alpha + beta transus temperature. Alpha phase hot forging may also be performed. Examples of such processing techniques are described in U.S. Patent Specification No. 3,645,800.

It has been reported that various properties of Zircaloy alloy components can be improved if beta treating is performed on the final size product or near final size product, in addition to the aforementioned conventional beta treatment that occurs early in the processing. Examples of such reports are as follows: United States Patent Specification No. 3,865,635 and United States Patent Specification No. 4,238,251. Included among these reports is the report that good Zircaloy-4 alloy corrosion properties in high temperature steam environments can be achieved by retention of at least a substantial portion of the precipitate distribution in two dimensional arrays, especially in the alpha phase grain boundaries of the beta treated microstructure. This configuration of precipitates is quite distinct from the substantially random array of precipitates normally observed in alpha worked (i.e. below approximately 1450°F) Zircaloy final product where the beta treatment, if any, occurred much earlier in the breakdown of the ingot as described above. The extensive alpha working of the material after the usual beta treatment serves to break up the two dimensional arrays of precipitates and distribute them in the random fashion typically observed in alpha-worked final product.

observed in final product according to the present invention that the average precipitate size has been reduced substantially below that observed in conventionally processed alpha worked product. It has been found that if 5 these subsequent alpha working and annealing temperatures are limited to below approximately 600 to 625°C that intermediate and final product having precipitate sizes significantly below that observed in conventionally processed Zircaloy are produced. Articles, thus processed 10 have been found to exhibit significantly lower corrosion weight gains in comparison with conventionally processed material in high temperature steam tests.

In order that the invention can be more clearly understood, convenient embodiments thereof will now be 15 described, by way of example, with reference to the accompanying drawings in which:

Figure 1 shows a flow diagram of a process according to one embodiment;

Figures 2A, B, C, D, E and F show transmission 20 electron microscopy photomicrographs showing the typical precipitate distribution and size observed in an article of another embodiment; and

Figure 3 shows a graph of the stress rupture properties of Zircaloy-4 stress relieved tubing processed 25 in accordance with the present invention compared to stress relieved tubing conventionally processed.

Material from a heat of nuclear grade Zircaloy-4 material was fabricated as shown in the process outline flow diagram of Figure 1. A Zircaloy-4 ingot having the 30 chemistry shown in Table I was broken down by conventional techniques to billets of approximately six inches in diameter. One of these billets was then given a beta treatment 1 which comprised holding it in a furnace set at about 1052°C (1925°F) for 1.5 hours and then water quenching it. At this point, it was prepared as usual for 35 extrusion. The hollow Zircaloy-4 billet was then heated to from 600-625°C and extruded to an extrusion having an

step 5, and then cold pilgered to a 1.25 inch outside diameter and a 0.2 inch wall thickness in step 6. The tube shell then received another intermediate anneal, step 7, identical to the step 5 intermediate anneal. It was 5 then further cold pilgered in step 8 to a 0.7 inch outside diameter, 0.07 inch wall thickness tube shell, and then annealed again (step 9) as in steps 5 and 7. The tube shell then received a final cold pilgering pass in step 10 to produce a 0.423 inch outside diameter and a 0.025 inch 10 wall thickness. A portion of this material then received a final anneal (step 11) of 7.5 hours at 466°C (870°F) to stress relieve the material. Another portion of this material received a full recrystallization anneal (step 11) at 550°C for 2 hours.

15 Thin foils were prepared from both the stress relief annealed material and the fully recrystallized material and evaluated via TEM (transmission electron microscopy). The stress relieved material contained dense networks of dislocations making it difficult to assess the 20 size and distribution of precipitates in the material. The precipitates, however, were observable in the fully recrystallized material and were found to be substantially, randomly distributed throughout the alpha matrix. Typical microstructures observed are shown in Figures 2A 25 (60,000X), 2B (60,000X), 2C (4600X), 2D (8000X), 2E (10,000X) and 2F (17,000X). Precipitate size was also measured and found to average about 0.077 microns (770 angstroms) with a standard deviation of about 0.035 microns. Precipitate size measurements performed on 30 another section of tubing produced an average precipitate diameter of about 500 angstroms. These observations show that material processed in accordance with the present invention possess a reduced precipitate size compared to that observed in conventionally processed Zircaloy. This 35 improvement in precipitate size is believed to be due to the lower extrusion, intermediate anneal and final anneal temperatures utilized after beta treatment, in combination

TABLE I

Composition of Zircaloy-4 Heat Processed
in Accordance with the Present Invention*

| <u>Element</u> | | | | | |
|----------------|-------|----------|----------------------------|----------|--------|
| 5 | Sn | 1.49 | w/o | | |
| | Fe | 0.21 | w/o | | |
| | Cr | 0.11 | w/o | | |
| | Fe+Cr | 0.33 | w/o | | |
| 10 | O | 1130 ppm | | (1350)** | |
| | | | <u>Impurities (in PPM)</u> | | |
| | Al | 55 | W | 25 | Ni 35 |
| | B | 0.2 | H | 5 (14) | Pb 25 |
| | C | 147 | Hf | 66 | Cb 50 |
| | Cd | 0.2 | Mg | 10 | Si 82 |
| 15 | Cl | 5 | Mn | 25 | Ta 100 |
| | Co | 10 | Mo | 10 | Ti 25 |
| | Cu | 22 | N | 23 (37) | U 0.8 |
| | | | | V | 25 |

*Average of analyses taken from a number of positions on
20 the ingot.

**Analyses in parentheses were performed on a TREX.

Claims:

1. An article of Zircaloy alloy material having a region of microstructure adjacent a surface of the article characterized in that, said region of microstructure comprises a substantially random distribution of precipitates, and said surface exhibits an adherent oxide film after five days exposure to 454°C, 10.3 MPa steam.
2. An article according to claim 1, characterized in that the precipitates have an average size below approximately 1100 angstroms.
3. An article according to claim 1 or 2, characterized in that the precipitates have an average size below approximately 800 angstroms.
4. An article according to claim 3, characterized in that the average precipitate size is below approximately 500 to 770 angstroms.
5. An article according to any of claims 1 to 4, characterized in that the microstructure further comprises a tangle of dislocations.
6. An article according to any of claims 1 to 4, characterized in that the microstructure further comprises polygonal alpha grains.
7. An article according to any of claims 1 to 4, characterized in that, the material further comprises an anisotropic crystallographic texture.
8. An article according to claim 7, characterized in that the material comprises precipitates in a matrix of alpha phase material which has the anisotropic crystallographic texture.

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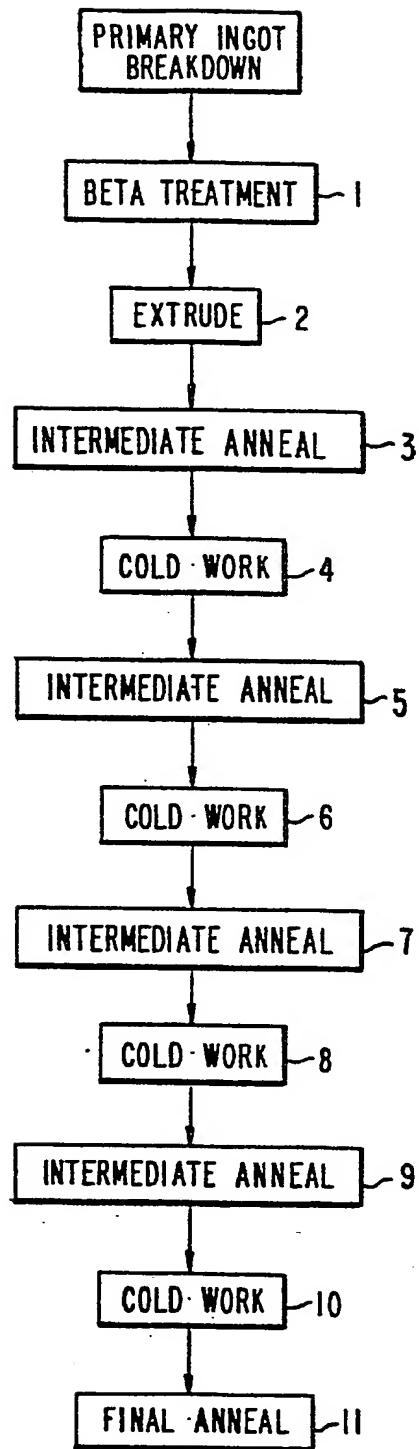


FIG. I

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FIG. 2C



FIG. 2D



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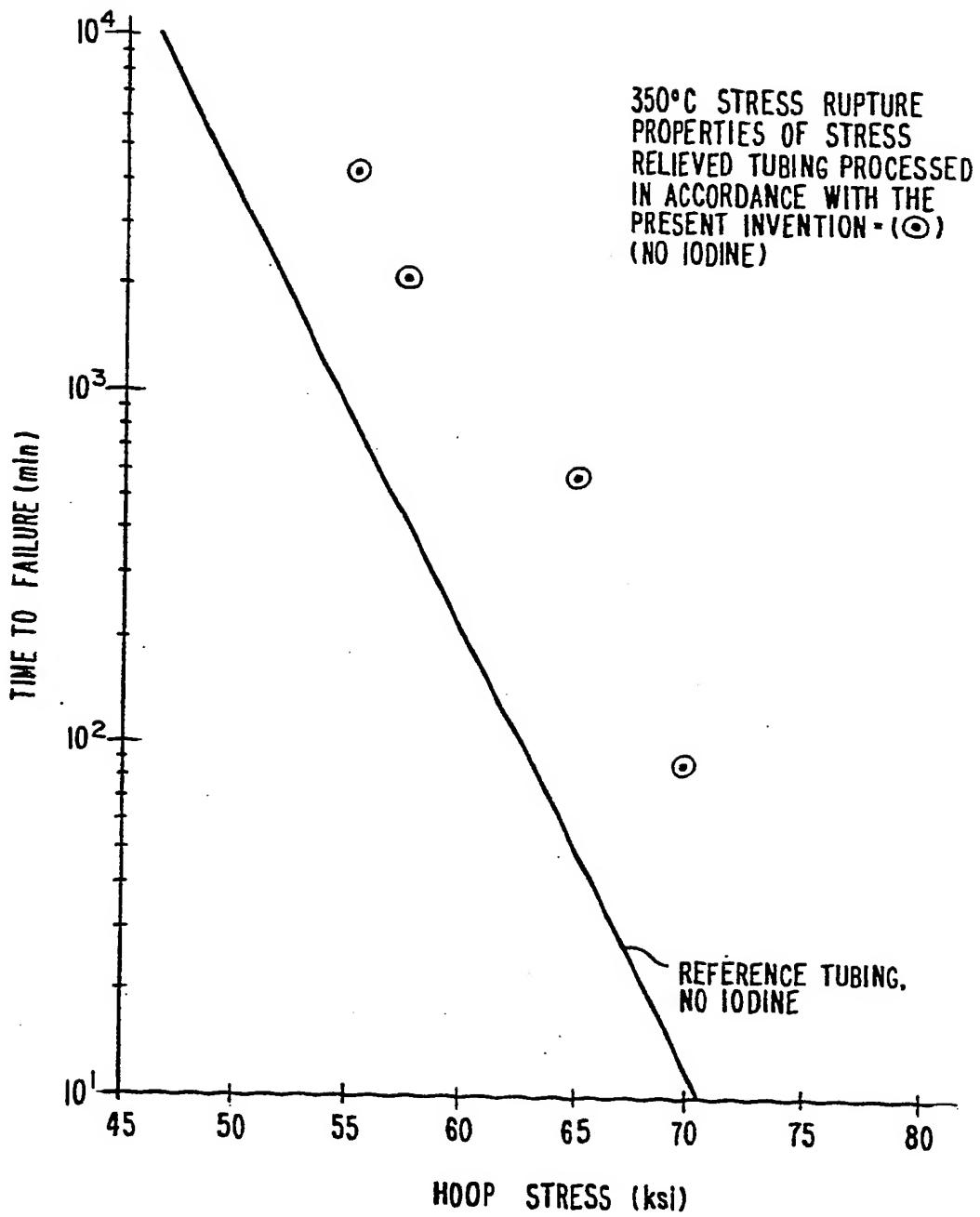


FIG. 3



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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|-------------------|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. *) |
| X | US-A-4 000 013 (MAC EWEN et al.) * Claims 1,2,4; column 2, line 66 - column 3, line 23 * | 1,10, 11 | C 22 F 1/18 |
| Y | US-A-3 431 104 (KLEPFER) * Claims 1-3; column 3, line 29 - column 4, line 9 * | 1,10 | |
| Y | BE-A- 691 169 (WESTINGHOUSE ELECTRIC CORP.) * Abstracts 1,3,6,7 * | 1,10 | |
| A | US-A-3 567 522 (THOMAS et al.) * Claims 1,3 * | 1,10, 11 | |
| A | FR-A-1 415 082 (NATIONAL DISTILLERS AND CHEMICAL CORP.) * Abstracts 1,2b,c,d,3 * | 1 | TECHNICAL FIELDS SEARCHED (Int. Cl. *) C 22 F 1/18 C 22 C 16/00 |
| The present search report has been drawn up for all claims | | | |
| Place of search | Date of completion of the search | Examiner | |
| THE HAGUE | 02-06-1983 | LIPPENS M.H. | |
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